Phase Equilibria

Chemistry for Petroleum Engineer – II

Foundation of chemistry - II

Phase Reactions, Number of phases, Components, intensive & extensive properties, and degrees of freedom, Introduction to phase diagrams

Properties can be divided into two types:

1. **Intensive properties**: These are independent of the mass or size of the system, for example, the pressure, the temperature, concentration, density, refractive index, molar entropy are all intensive variables.
2. **Extensive properties**: Properties that depend on the amount of the material in the phase such as weight, volume, heat capacity.
3. **The phase rule** is concerned ONLY with **intensive** variables of a system in a state of *equilibrium.*
4. *The phase rule applies to all macroscopic systems which are in a state of heterogeneous equilibrium and which are influenced only by changes in pressure, temperature, and concentration.*

Basic definitions

1. **The System:** is defined as a substance or a mixture of substances isolated in some way from the rest of the world.

   The effects of P, T, and the properties of the constituents on the *physical state* of the materials present in the system can then be investigated.

   Note that the properties of the system depends on P,T and composition.

2. **The phase**: that part of a system which is chemically and physically uniform throughout .Usually given the letter **P**

   e.g. a solution in which there are two chemical species (or more) – one phase

   Two immiscible liquid – two phase

3. **Components:** (usually given letter C) defined as the least number of independent *substances*, which must be specified so that the composition of each and every phase is described. Notice – we do not speak of species .

   (H^+, OH^-, Na^+ etc are species and not substances.)

4. The **variance also know as degree of freedom**, F, of a system is the number of *intensive* variables that can be changed independently without disturbing the number of phases in equilibrium.

- In a single-component, single-phase system ($C = 1$, $P = 1$), the pressure and temperature may be changed independently without changing the number of phases, so $F = 2$. We say that such a system is **bivariant**, or that it has two **degrees of freedom**. On the other hand, if two phases are in equilibrium (a liquid and its vapour, for instance) in a single-component system ($C = 1$, $P = 2$), the temperature (or the pressure) can be changed at will, but the change in temperature (or pressure) demands an accompanying change in pressure (or temperature) to preserve the number of phases in equilibrium. That is, the variance of the system has fallen to 1.

Homogeneous & Heterogeneous Equilibrium

- A system may be considered homogeneous when it is uniform throughout its volume, so that its properties are the same in all parts ,

  a solution of sodium chloride is homogeneous
- Any equilibrium occurring in a homogeneous system is termed a homogeneous equilibrium, for example an equilibrium involving methyl acetate, acetic acid, and methyl alcohol when these are all in solution.

- A heterogeneous system consists of two or more distinct homogeneous regions. Thus ice and water or carbon tetrachloride and water are both heterogeneous systems. The homogeneous regions or phases are separated from one another by surfaces or interfaces at which occur sudden changes in physical properties
- **For a system to be in heterogeneous equilibrium it must be in thermal, mechanical and chemical equilibrium.**

- 1. **Thermal equilibrium** exists when there is no flow of heat from one part of a system to another. From experience, this is known to mean that the two parts are at the same temperature. This cannot be proved but is a fact of nature and considered of such fundamental importance to thermodynamics that it is referred to as the Zeroth law. For two phases, α and β, therefore, the requirement is:

$$T_\alpha = T_\beta$$

- **Mechanical equilibrium** exists when the pressure is constant throughout all parts o Thus for two phases, α and β

This is established from thermodynamics as a criterion of equilibrium in closed systems at constant temperature and composition.

$$P_\alpha = P_\beta$$

3. **Chemical equilibrium** of the system exists when the rate of each forward reaction equals the rate of the corresponding backward reaction. Thus there must be a dynamic reversible interchange of matter between the various parts of the system. The chemical potential of a particular species must be uniform in all parts of the system, a fact which may be established from the thermodynamics of a closed system in equilibrium. In terms of the Gibbs Free Energy, G, the condition for equilibrium is given by $(dG)_{T,P} = 0$. Suppose that two parts of a system contain a substance which has chemical potential $\mu\alpha$ in one part and $\mu\beta$ in the other. If, at equilibrium d*n* moles of that substance change from α to β, then:

$$(\mathrm{d}G)_{T,P} = -\,\mu_\alpha.\mathrm{d}n + \mu_\beta.\mathrm{d}n = 0$$

From which:

$$\mu_\alpha = \mu_\beta$$

Conditions for equilibrium…cont

- The three conditions outlined must apply not only within each phase but also between the phases. For example, if ice and liquid water are in equilibrium, the chemical potential of the ice must equal the potential of the liquid water.

Number of components- How do we find them

- Consider ***each*** phase. Deduce the substances that could be used to make up, or are in, each phase. Include only a set of *independent* substance in each phase.
- Consider ***every*** phase. Form a list of the substances in all the phases, and count the number of independent substances in the system.e.g.

1. An aqueous solution of sucrose . This is one phase but it has two components.
2. Aqueous solution of sucrose , its equilibrium vapour, which is water vapour, and solid sucrose in equilibrium with the solution

Now we must deal with ***each*** and ***every*** part of the definition

Vapour:	water
Liquid:	water and sucrose
Solid:	sucrose

The substances needed to describe all the phases are water and sucrose.. Therefore, C=2

- Examples on calculating C,P and F
- In the ice/water/water vapour system, each phase may be made up using only one chemical substance, H_20. There is only one component.

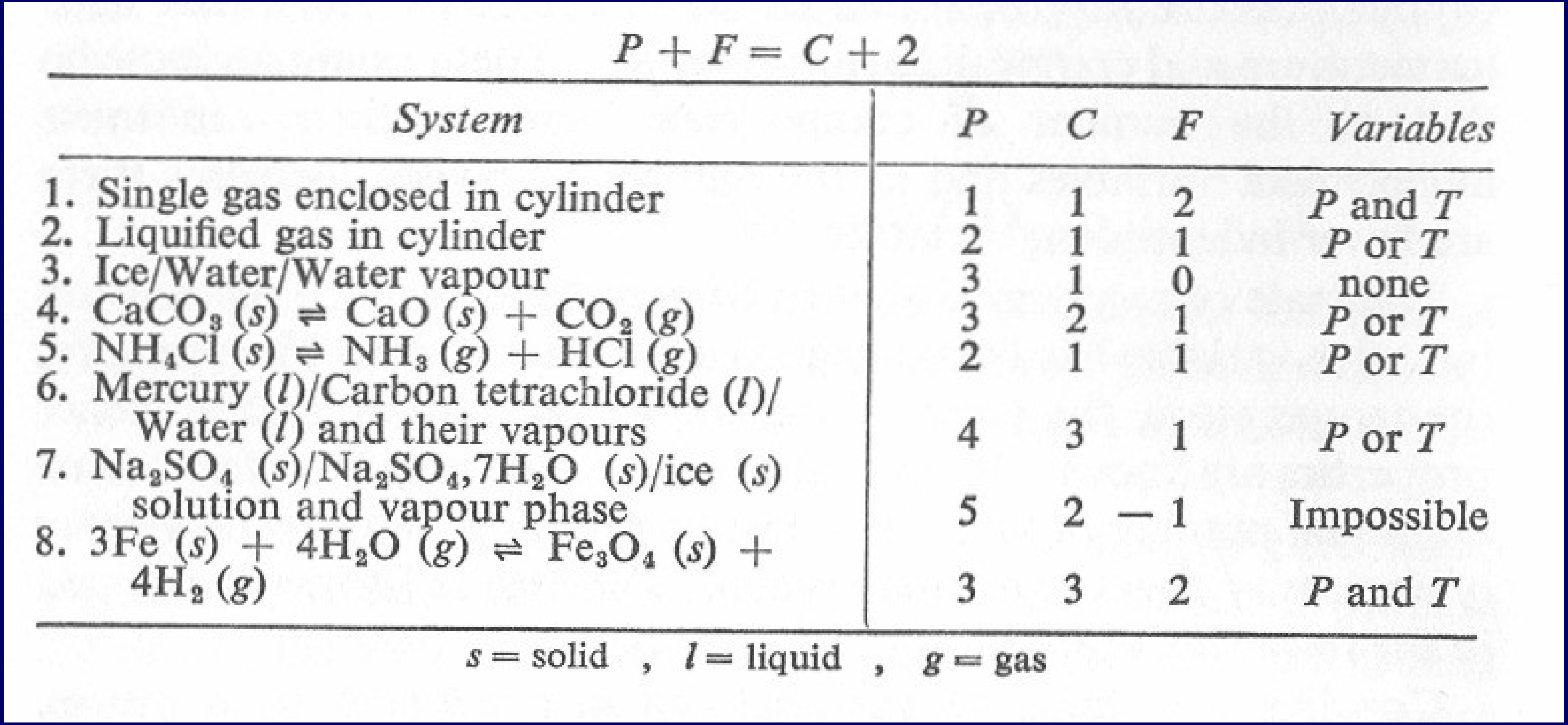
$$CaCO_3 \text{ (solid)} \rightleftharpoons CaO \text{ (solid)} + CO_2 \text{ (gas)}$$

- There are three phases in this system. Now obviously by using the three elements calcium, carbon and oxygen, all of the phases could be made, but this would also be possible using the chemical substances calcium oxide and carbon dioxide. The least number of substances is therefore two, C = 2.
- Consider the system which has as possible phases Na_2SO_4, $Na_2SO_4.7H_2O$, $Na_2SO_4.l0H_2O$, Na_2SO_4 solution, solid ice and water vapour. Each phase may be made using sodium sulphate and/or - water, that is, the composition of each phase may be expressed in terms of the chemicals Na_2SO_4 or H_20 or both. This system is therefore two component and C = 2.

Solid ammonium chloride NH_4Cl, and its equilibrium vapour, which cab be shown to consist of equimolar amounts of $NH_3$and HCl. How many components?

- Solid NH_4Cl Vapour: NH_3 and HCl in equimolar amounts
- Solid consist of 1 substance.
- Vapour consists of two substances BUT THEY ARE NOT INDEPENDENT.
- Compounds in the vapour phase can be gotten from the solid.
- The system has C=1

The Phase Rule



$$P + F = C + 2$$

System	P	C	F	Variables
1. Single gas enclosed in cylinder	1	1	2	P and T
2. Liquified gas in cylinder	2	1	1	P or T
3. Ice/Water/Water vapour	3	1	0	none
4. $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$	3	2	1	P or T
5. $NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$	2	1	1	P or T
6. Mercury (l)/Carbon tetrachloride (l)/ Water (l) and their vapours	4	3	1	P or T
7. Na_2SO_4 (s)/$Na_2SO_4,7H_2O$ (s)/ice (s) solution and vapour phase	5	2	− 1	Impossible
8. $3Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$	3	3	2	P and T

s = solid , l = liquid , g = gas

Revision :Degrees of freedom F

- Intensive property: properties that are independent of the amount like density, temperature, refractive index, molar heat capacity …etc.
- Extensive property: depend on the amount of the material in the phase such as weight, volume,
- **The number of degrees of freedom of a system is defined as** : The least number of ***intensive*** variables that must be specified to fix the values of all the remaining ***intensive*** variables
- **Phase Reaction**: A chemical or physical effect which introduces or removes a phase.

What is a “Phase”?

- A phase is a homogenous, physically distinct and

  mechanically separable portion of the material with a given chemical composition and structure.

- For solids: Chemically and structurally distinct
- For liquids: Miscibility
- For gases: Always 1 phase

Derivation of the phase rule

- Clearly, for a one-component system, pressure and temperature are the only intensive variables. For a system in which one phase contains two components, however, there is an additional variable—the ratio of the two components in that particular phase.
- Generally, if there are C components in one phase there must be (C — 1) composition variables. For a system of P phases there must be P (C — 1) such variables. Now the pressure and temperature variables will be the same throughout the system, so that the total is:

$$P\,(C-1)+2$$

Derivation of the phase rule.....cont

- when equilibrium exists, the chemical potential of a component must be the same in any part of the system. For one component in two phases α and β, $\mu\alpha = \mu\beta$ and in three phases, α, β and γ there will be two equations $\mu\alpha = \mu\beta$ and $\mu\alpha = \mu\gamma$. In general, for P phases, it would be possible to write (P — 1) equations for each component. For C components the number of equations
- must be

$$C\,(P - 1)$$

Derivation of the phase rule…… cont

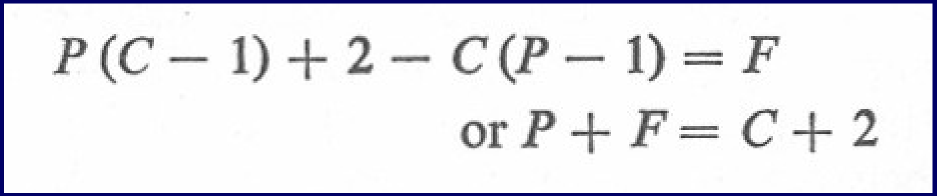
- Referring now to the algebra of simultaneous equations, it is well known that a complete solution for three variables is only possible if three equations are available, as in the example below:

$$\begin{aligned} x + 2y + z &= 8 \\ 2x + y + z &= 7 \\ x + 3y + 3z &= 16 \end{aligned}$$

- If the last equation were not given, a complete solution is not possible. However, an arbitrary value could be given to x and values for y and z then calculated. These values would then depend on the value chosen for x, the independent variable. If there were six variables and only three equations, then three of the variables would be independent. Generally (No. of variables) — (no. of equations) = no. of independent variables.

Derivation of the phase rule...... cont

- Apply this rule to the terms derived in F and C, and let the number of independent variables be F.



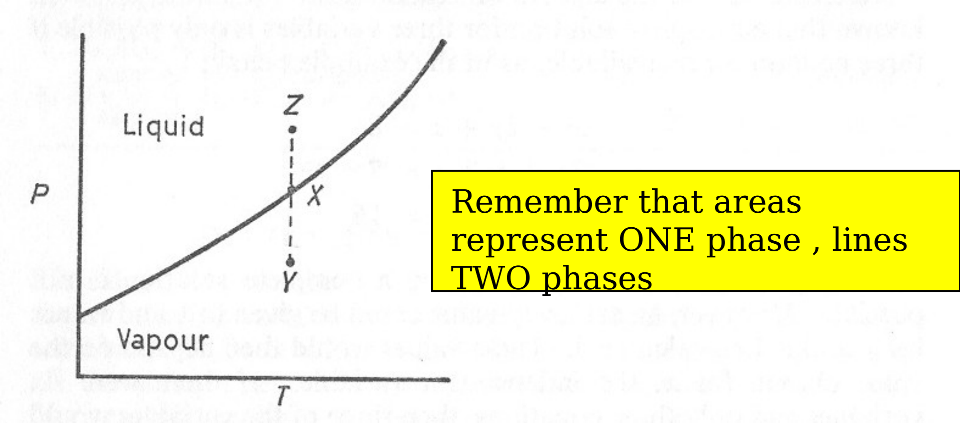
$$P(C-1)+2-C(P-1)=F$$

$$\text{or } P+F=C+2$$

- As an example, the meaning of F = 0 should now be more evident. There are enough equations to allow complete solution for all the variables. The system is thus completely defined or invariant.
- In this derivation of the Phase Rule it has been assumed that every component is present in every phase. This is not necessarily true, as was seen in the treatment of the calcium carbonate system, If a particular component is absent from one phase, then the number of component variables is reduced by one.

PHASE EQUILIBRIUM DIAGRAMS

The system water/water vapour for which P = 2 and C = 1, is univariant, F = 1. Thus at a chosen temperature, the vapour pressure is fixed. When plotted on P — T coordinates, the saturated vapour pressure curve of water results,



Remember that areas represent ONE phase , lines TWO phases

At point X, corresponding to a particular temperature, water and its vapour are in equilibrium. If the pressure is increased to Z, the vapour condenses and the system becomes one liquid phase. If the pressure is reduced to Y, the water boils and the system again becomes a single phase. The area above the curve represents a single liquid phase and that below the curve a single gaseous phase.

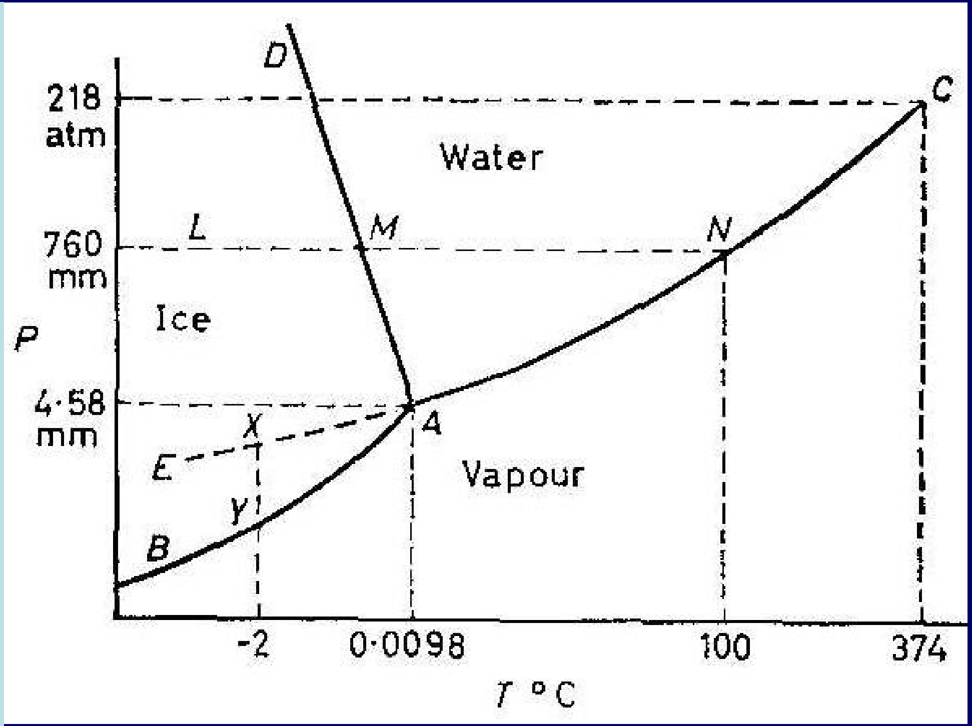
While two phases coexist, however, the variation must be confined to the curve itself, the boundary between the liquid and vapour

One Component Phase Diagram

- The simplest case-Water . Also known as a **P-T diagram**
- In all phase diagrams one must know the following:
- Sign of [dP/dT] for:
    - Solid-Liquid line equilibria
    - Liquid-Gas line equilibria
    - Gas-Solid line equilibria

What is required to draw the phase diagram?

The complete pressure-temperature diagram is : constructed from
The vapour pressure (1) .curve for the liquid
The vapour pressure (2) .curve for the solid
The melting point curve (3) as a function of pressure.
(4) Data for the solid—liquid—vapour equilibrium .point
Data for solid-phase (5) .transitions



ne AD has two important features. Its slope shows
hat an increase of pressure will lower the melting point of ice
ince water expands on freezing, Le Chatelier’s principle
redicts the above result and a quantitative assessment
the effect is made later in our lectures using the
lausius-Clapeyron equation. On AD is the true
elting point of ice, 0.0023°C at 760 mm pressure.
he thermometric standard, 0°C, refers
o the freezing point of water saturated with air at 760mm
essure. Three Phases in Equilibrium at point (A).

P_T Diagram of water

- Line AD has two important features. Its slope shows that an increase of pressure will lower the melting point of ice. Since water expands on freezing, Le Chatelier’s principle predicts the above result. On AD is the true melting point of ice, 0.0023°C at 760 mm pressure. The thermometric standard, 0°C, refers to the freezing point of water saturated with air at 760mm pressure.

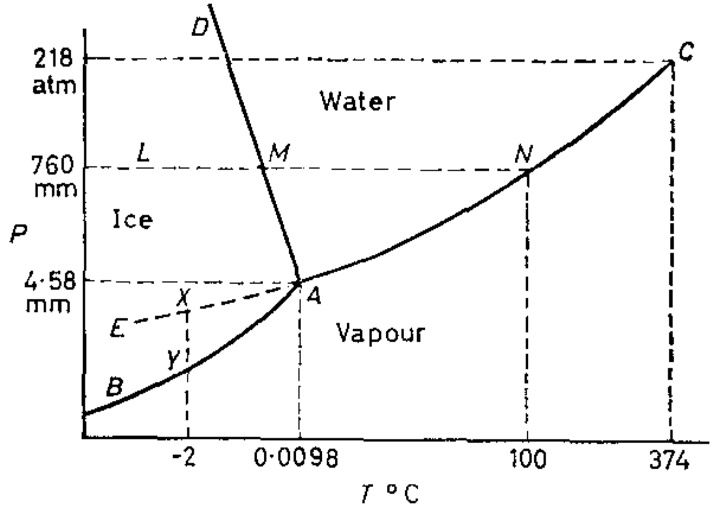


Figure 2. The water system

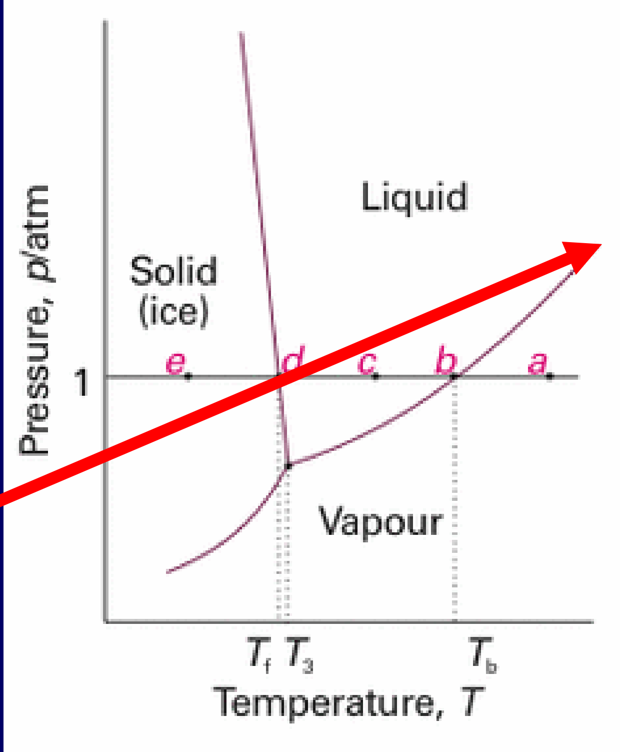
- Three phases
- At point A, solid, liquid and vapour are in equilibrium. At this one temperature ice and water have the same fixed vapour pressure and the system is invariant. This is the Triple Point, 0-0098°C and 4-58 mm pressure, where F 0. This point is a fundamental constant for the water system and its values cannot be changed in any way. It is so accurately defined (± 00001°C) that it is now used as a fixed point on the International Temperature Scale rather than the melting point of ice under atmospheric conditions.

Single phase is represented by an AREA

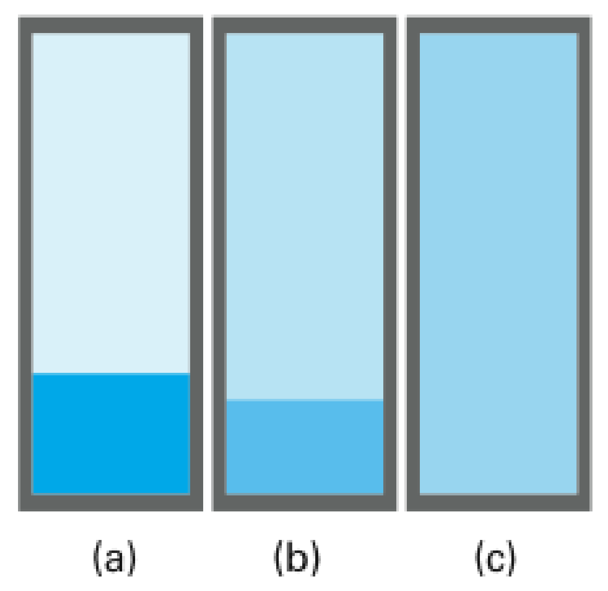
Two phases are represented by a line

Three phases are represented by a point

Critical point:: the temperature at which boundaries (surfaces) disappear



The vapour pressure at the critical temperature is called the critical pressure, P_c. At and above the critical temperature, a single uniform phase called a supercritical fluid fills the container and an interface no longer exists. That is, above the critical temperature, the liquid phase of the substance does not exist



$P+F=C+2$

- In one-component systems there may be one, two or three phases in equilibrium.

Applying the Phase Rule for $C = 1$

- When p 1, F 2, that is, the system is ***bivariant***
- When $P = 2$, $F = 1$, the system is ***univariant*** When $P = 3$, $F = 0$, the system is ***invariant.***
- The three cases are best illustrated by the use of specific examples.

IMPORTANT

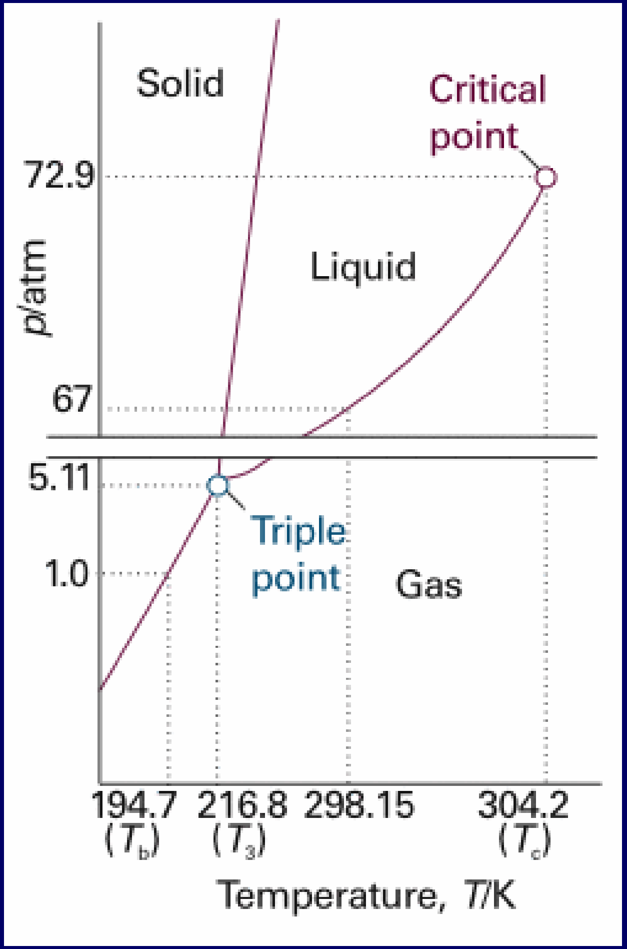
- THE PHASE RULE IS ALSO KNOWN BY THE NAME:

GIBBS PHASE RULE

$$F+P=C+2$$

(a) **The phase diagram for carbon dioxide.**

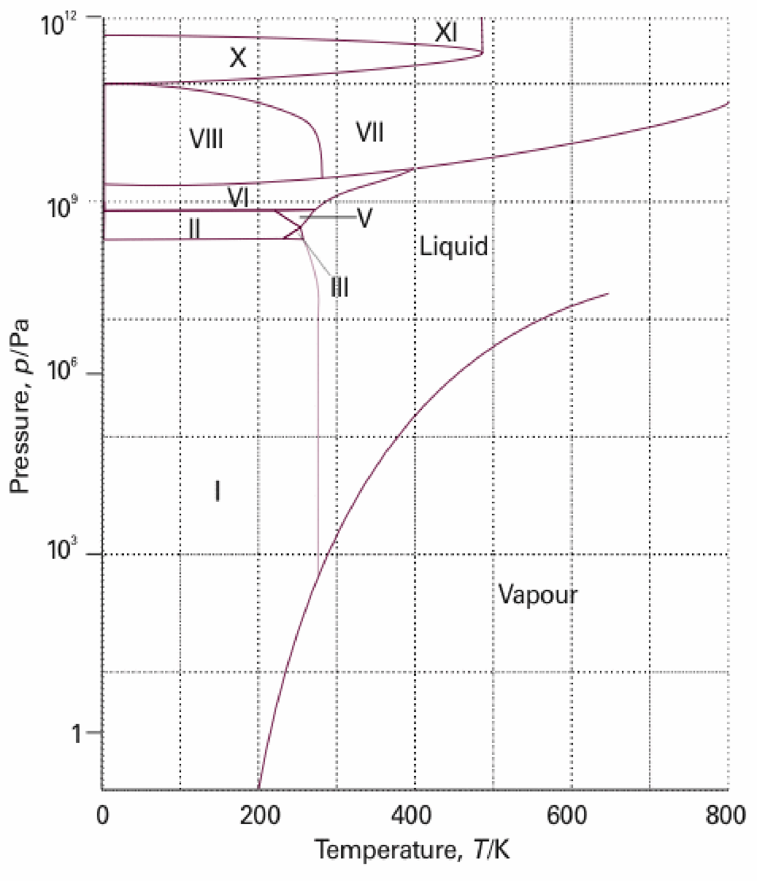
- The features to notice include the positive slope of the solid–liquid boundary (the direction of this line is characteristic of most substances), which indicates that the ***melting temperature*** of solid carbon dioxide rises as the *pressure* is increased.
- Notice also that, as the *triple point* lies above 1 atm, the liquid **cannot exist** at normal atmospheric ***pressures*** whatever the temperature, and the solid sublimes when left in the open (hence the name ‘dry ice’). To obtain the liquid, it is necessary to exert a pressure of at least 5.11 atm. Cylinders of carbon dioxide generally contain the liquid or compressed gas; at 25°C that implies a vapour pressure of 67 atm if both gas and liquid are present in equilibrium.



- When the gas squirts through the throttle it cools by the Joule–Thomson effect, so when it emerges into a region where the pressure is only 1 atm, it condenses into a finely divided snow-like solid.

(b) Water – complete phase diagram

- The liquid–vapour boundary in the phase diagram summarizes how the vapour pressure of liquid water varies with temperature. It also summarizes how the boiling temperature varies with pressure: we simply read off the temperature at which the vapour pressure is equal to the prevailing atmospheric pressure. The solid–liquid boundary shows how the melting temperature varies with the pressure. Its very steep slope indicates that enormous pressures are needed to bring about significant changes.



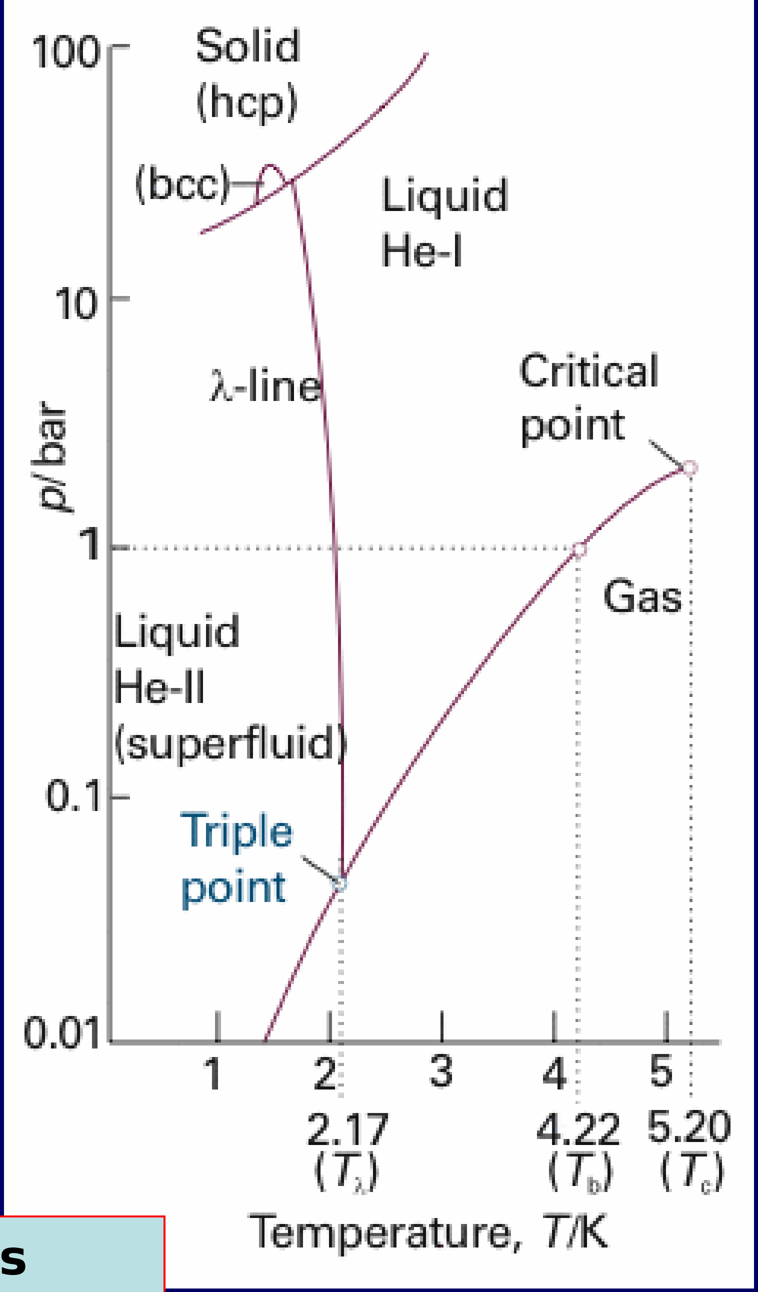
Pressure units are in Pascal Pa. 1 atm = 10^5 Pascal

1 atm = 101.325 kilo Pascal

- The sort of information which can be obtained from this phase diagram can be summarized as follows:
- *how the boiling temperature varies with pressure*
- *Variation of boiling point with pressure*
- *how the melting temperature varies with the pressure.*
- *that water has one liquid phase but many different solid phases other than ordinary ice Some of these phases melt at high temperatures. Ice VII, for instance, melts at 100°C but exists only above 25 kbar*
- There are six triple points – some ice solids melt above 100^{o}C
- The diagram shows **polymorphs**, or different solid phases

(C) Helium

- Helium behaves unusually at low temperatures. For instance, the solid and gas phases of helium are never in equilibrium however low the temperature: the atoms are so light that they vibrate with a large amplitude motion even at very low temperatures and the solid simply shakes itself apart. Solid helium can be obtained, but only by holding the atoms together by applying pressure.



Note the units used

- helium is the only known substance with a liquid–liquid boundary, shown as the **λ-line (lambda line)**
- The phase marked He-I in the diagram behaves like a normal liquid; the other phase, He-II, is a **superfluid**; it is so called because it flows without viscosity.

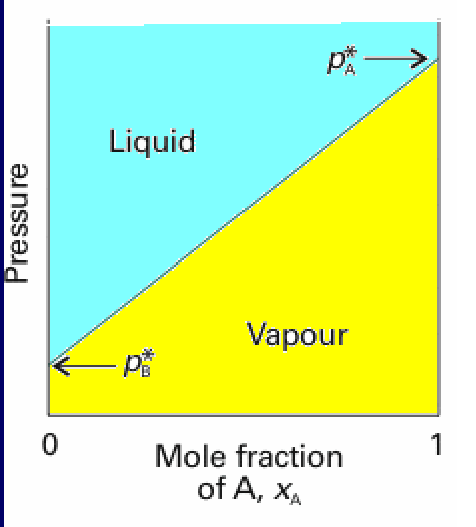
Two-component systems

- When two components are present in a system, $C = 2$ and $F = 4 - P$. If the temperature is constant, the remaining variance is $F' = 3 - P$, which has a maximum value of 2. (The prime on *F* indicates that one of the degrees of freedom has been discarded, in this case the **temperature**.) One of these two remaining degrees of freedom is the pressure and the other is the composition (as expressed by the mole fraction of one component).

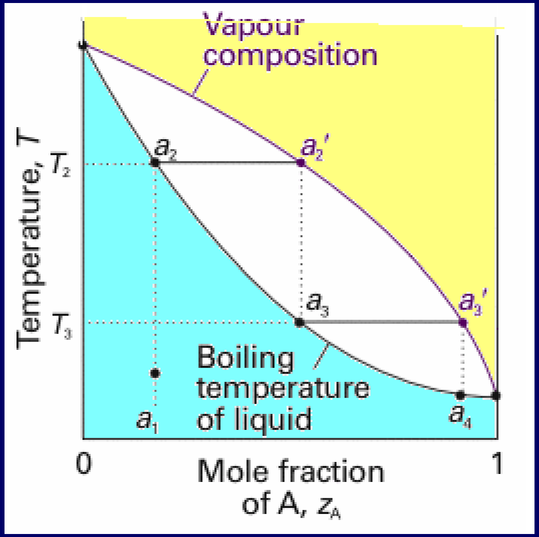
Two Types of Diagrams

- Type one:

1. pressures v compositions at constant T
2. temperature v composition at constant P



TYPE ONE

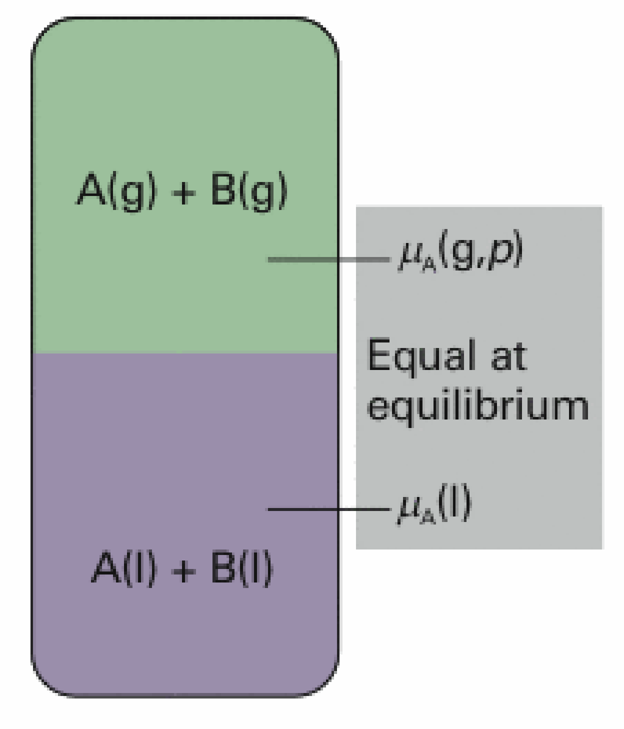


TYPE TWO

(a) Ideal solutions

- Because the chemical potential of a substance (A) in the vapour depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure.

- We shall denote quantities relating to pure substances by a superscript *, so the chemical potential of pure A is written μ_A^*,and as $\mu_A^*(l)$ when we need to emphasize that A is a liquid. Because the vapour pressure of the pure liquid is p_A^*,it follows that the chemical potential of A in the vapour (treated as a perfect gas) is $\mu_A + RT \ln p_A^*$(with p_A to be interpreted as the relative pressure p_A/p). These two chemical potentials are equal at equilibrium so we can write:



$$\mu_A^* = \mu_A^{\ominus} + RT \ln p_A^*$$

If another substance, a solute, is also present in the liquid, the chemical potential of A in the liquid is changed to μ_A and its vapour pressure is changed to p_A. The vapour and solvent are s we can write

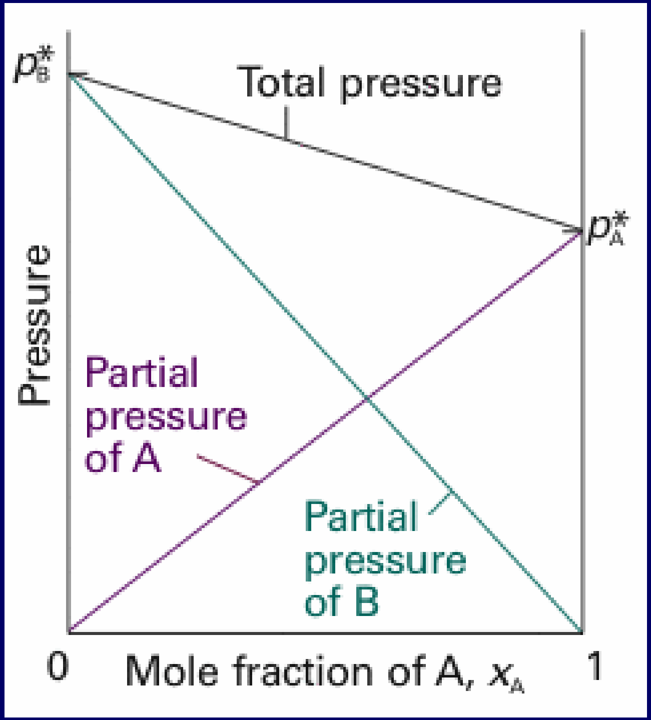
$$\mu_A = \mu_A^{\ominus} + RT \ln p_A$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas. To do so, we write as $\mu_A = \mu_A^* - RT \ln p_A^*$ and substitute this expression to obtain

$$\mu_A = \mu_A^* - RT \ln p_A^* + RT \ln p_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

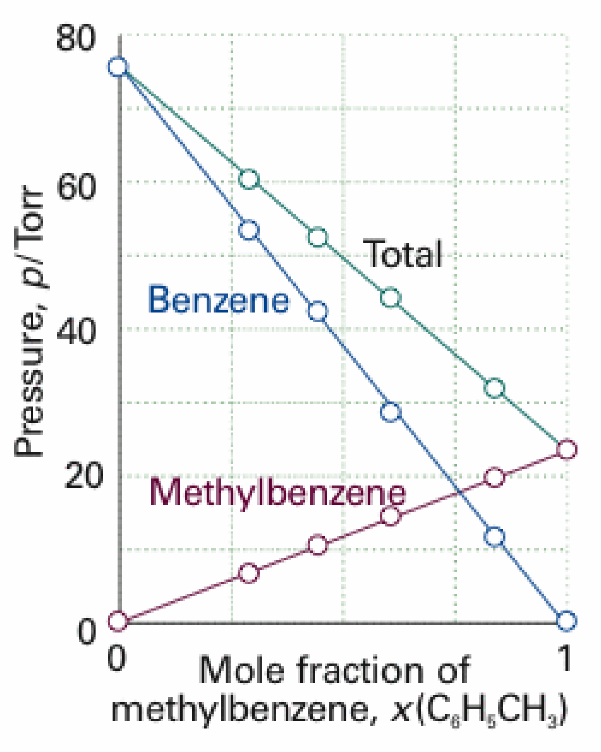
- Raoult found that the ratio of the partial vapour pressure of each component to its vapour pressure as a pure liquid, p_A/p_A^*, is approximately equal to the mole fraction of A in the liquid mixture. That is, what we now call **Rao**

$$p_A = x_A p_A^*$$



Gases

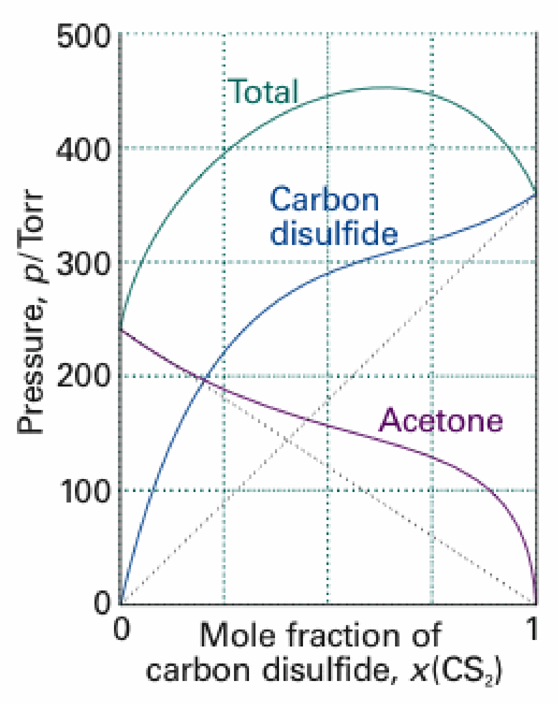
Liquids



- Solutions obeying Raoult’s law are termed ideal solution. For an ideal solution, we thus can write

$$\mu_A = \mu_A^* + RT \ln x_A$$

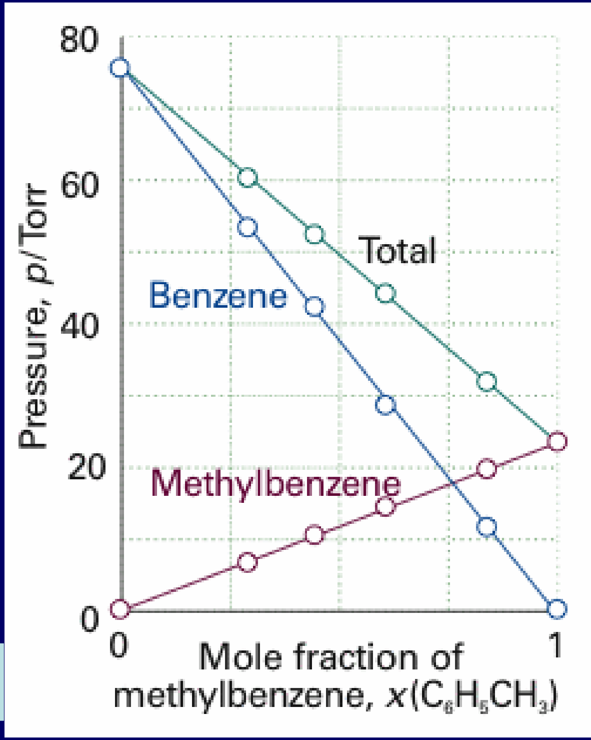
- Please note : (μ*) denotes chemical potential of the pure A.



Dissimilar liquids

Notice the way they obey Rauult’s law as they are very similar compounds (liquids).

Similar liquids



Let us look at two components systems

- When two components are present in a system, $C = 2$ and $F = 4 - P$. If the temperature is constant, the remaining variance is $F' = 3 - P$, which has a maximum value of 2. (T is fixed) One of these two remaining degrees of freedom is the pressure and the other is the composition (as expressed by the mole fraction of one component).
- Hence, one form of the phase diagram is a map of pressures and compositions at which each phase is stable. Alternatively, the pressure could be held constant and the phase diagram depicted in terms of temperature and composition. See the following diagram:

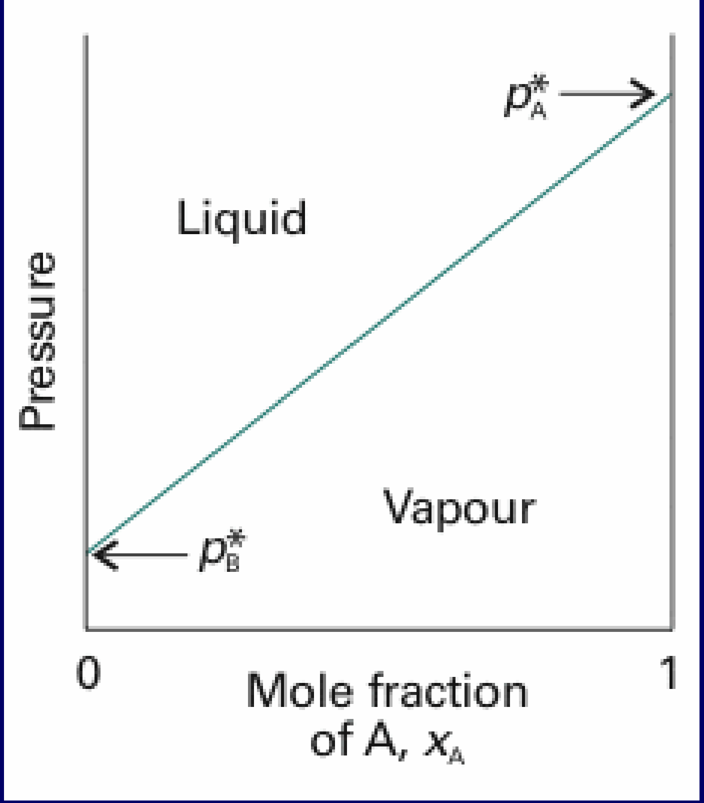
Vapour pressure diagrams

The partial vapour pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixtur

$$p_A = x_A p_A^* \qquad p_B = x_B p_B^*$$

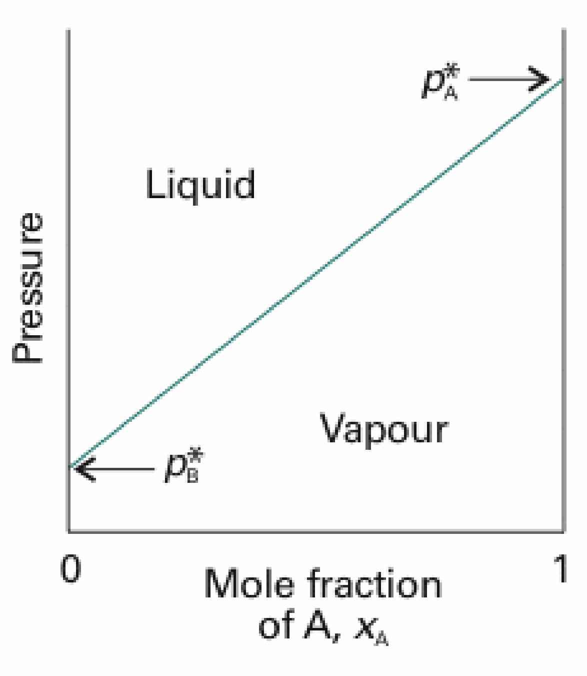
where p^*_A is the vapour pressure of pure A and p^*_B that of pure B. The total vapour pressure p of the mixture is therefore

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A$$



This diagram shows the variation of the total vapour pressure of a binary mixture with the mole fraction of A in the liquid when Raoult ’s law

- The last equation shows that the total vapour pressure (at some fixed temperature) changes linearly with the composition from p^*_B to p^*_A as x_A changes from 0 to 1.



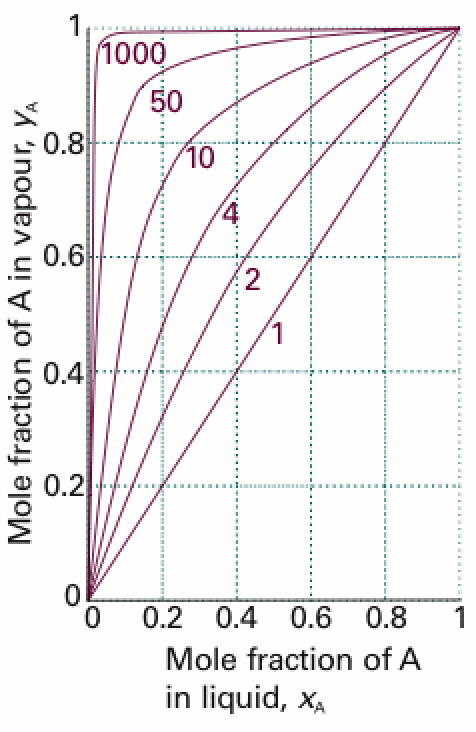
Vapour pressure diagrams Cont

(a) The composition of the vapour

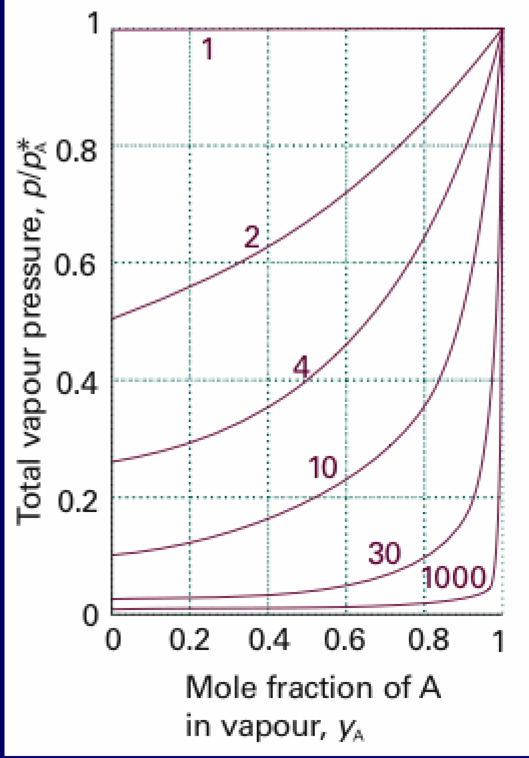
- The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This expectation can be confirmed as follows. It follows from Dalton’s law that the mole fractions in the gas, y_A and y_B, are

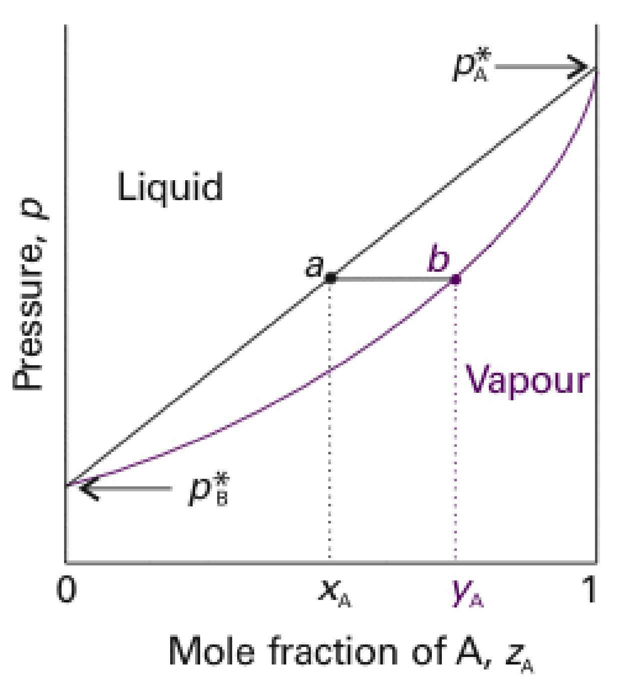
$$y_A = \frac{p_A}{p} \qquad y_B = \frac{p_B}{p}$$

$$p_A = x_A p_A^* \qquad p_B = x_B p_B^*$$



These graphs can be obtained from the past equations. They are of no value to us as such. What if we combine these two figures into ONE

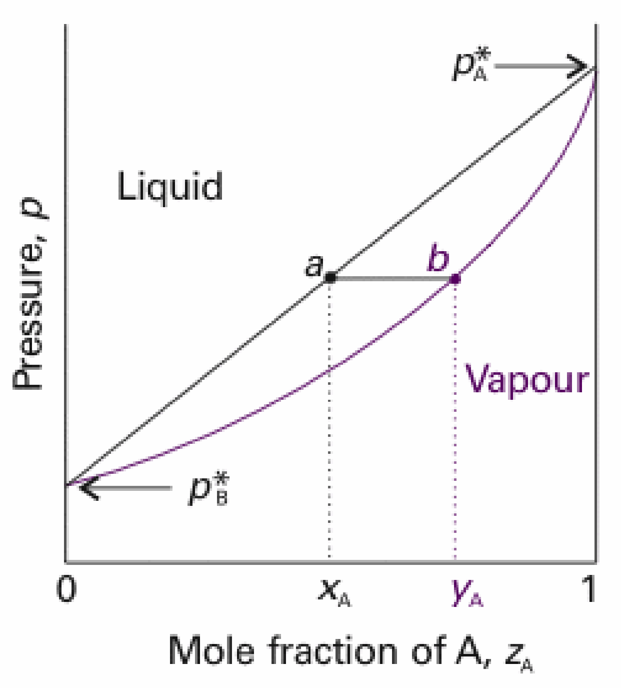




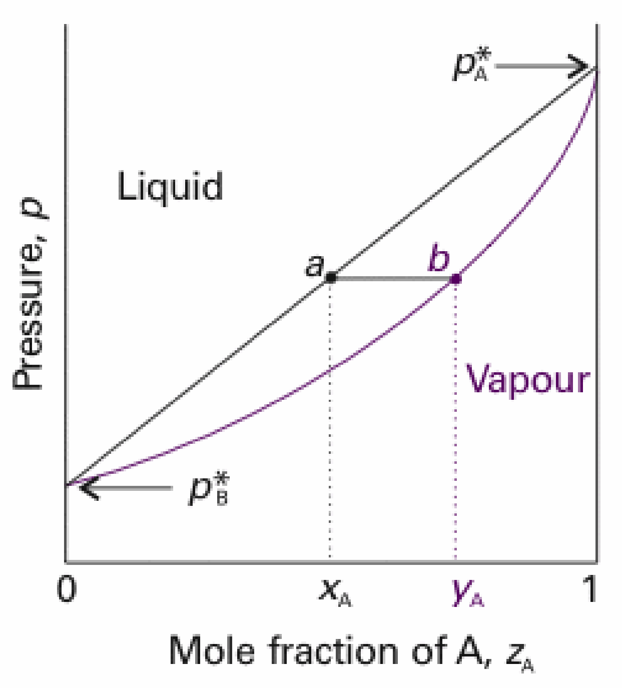
We obtain the figure on the left which shows the dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system. *A point between the two lines corresponds to both liquid and vapour being present*; outside that region there is only one phase present. The mole fraction of A is denoted z_A.

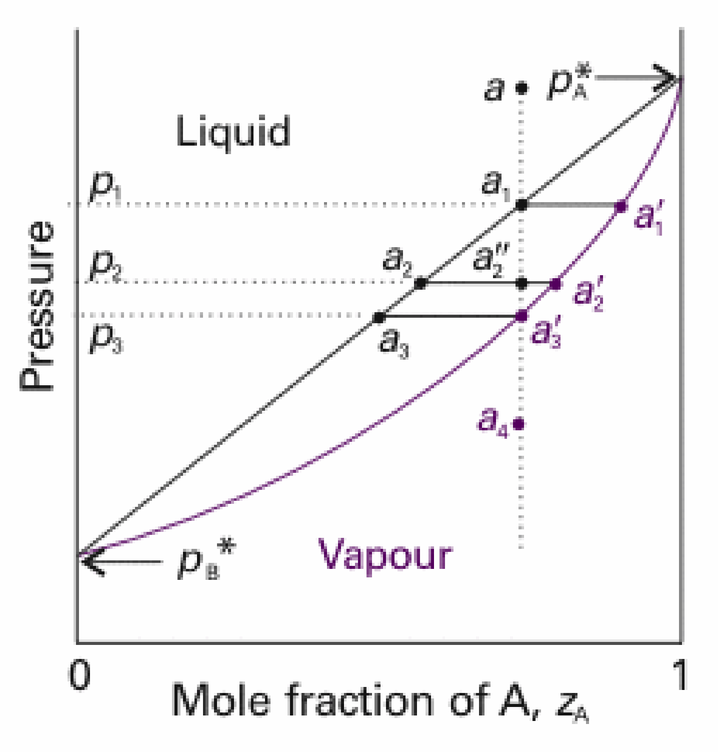
(b) The interpretation of the diagrams

The point *a* indicates the vapour pressure of a mixture of composition x_A,and the point *b* indicates the composition of the vapour that is in equilibrium with the liquid at that pressure. Note that, when two phases are in equilibrium, $P = 2$ so $F' = 1$ (as usual, the prime indicating that one degree of freedom, the temperature, has already been discarded). That is, if the composition is specified (so using up the only remaining degree of freedom), the pressure at which the two phases are in equilibrium is fixed



- Points that lie between the two lines correspond to a system in which there are two phases present, one a liquid and the other a vapour. To see this interpretation, consider the effect of lowering the pressure on a liquid mixture of overall composition *a*

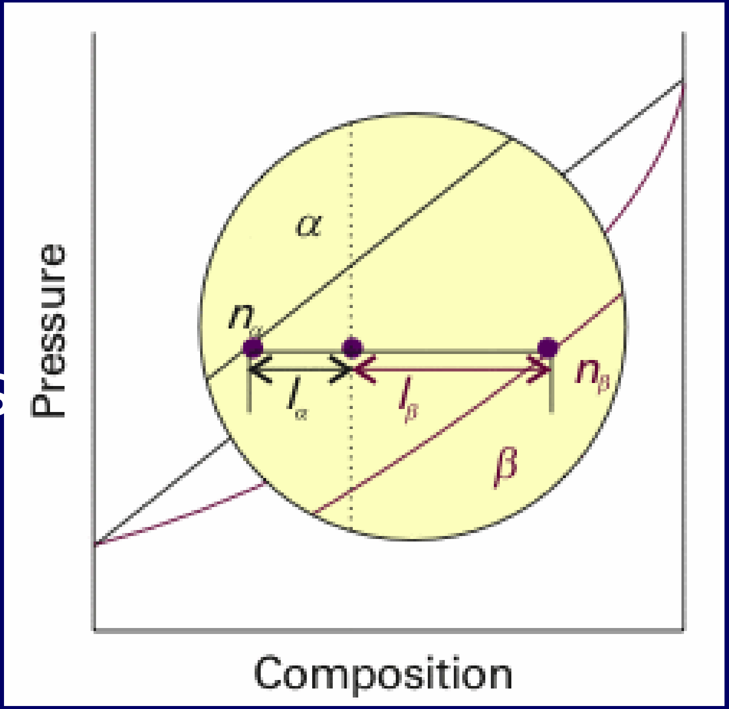




- The changes to the system do not affect the overall composition, so the state of the system moves down the vertical line that passes through *a*. This vertical line is called an isopleth, from the Greek words for ‘equal abundance’ .Until the point a_1 is reached (when the pressure has been reduced to p_1),the sample consists of a single liquid phase. At a_1 the liquid can exist in equilibrium with its vapour. As we have seen, the composition of the vapour phase is given by point a_1'. A line joining two points representing phases in equilibrium is called a **tie line**.

Tie-line or lever rule

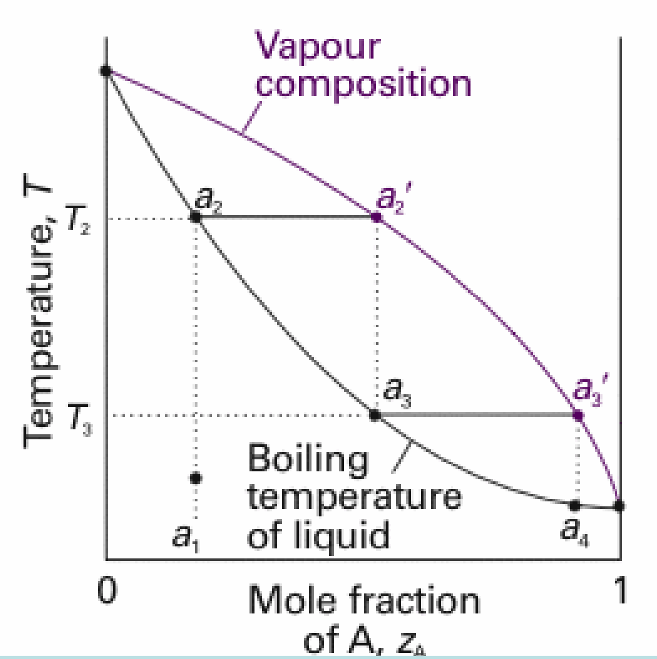
The distances $l\alpha$ and $l\beta$ are used to find the proportions of the amounts of phases α (such as vapour) and β (for example, liquid) present at equilibrium. The lever rule is so called because a similar rule relates the masses at two ends of a lever to their distances from a pivot $n_\alpha \times l_\alpha = n_\beta \times l_\beta$ for balance).



Temperature–composition diagrams

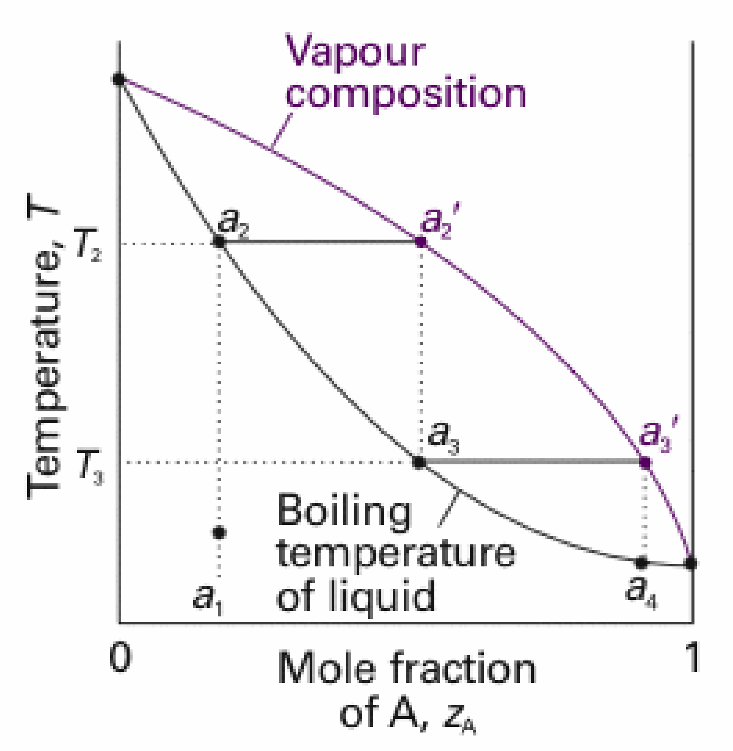
To discuss distillation we need a **temperature–composition diagram**, a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures (and a given pressure , typically 1 atm). An example is shown in adjacent figure. Note that the liquid phase now lies in the lower part of the diagram

$$F = C - P + 2$$



The temperature–composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boilings and condensations of a liquid originally of composition a_1 lead to a condensate that is

The temperature–composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boiling and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation technique is called fractional distillation.



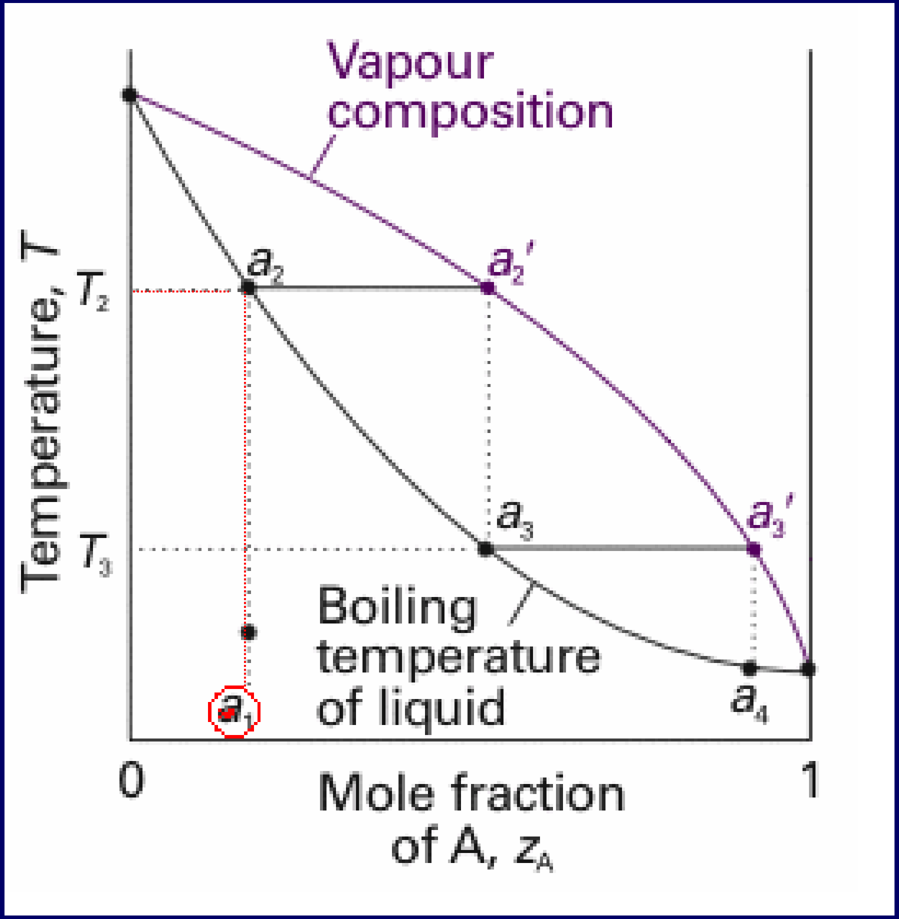
$$F = C - P + 2$$

(a) The distillation of mixtures

- The region between the lines in the past figure is a two-phase region where $F' = 1$. As usual, the prime indicates that one degree of freedom has been discarded; in this case, the pressure is being kept fixed, and hence at a given temperature the compositions of the phases in equilibrium are fixed. The regions outside the phase lines correspond to a single phase, so $F' = 2$, and the temperature and composition are both independently variable.

$$F = C - P + 2$$

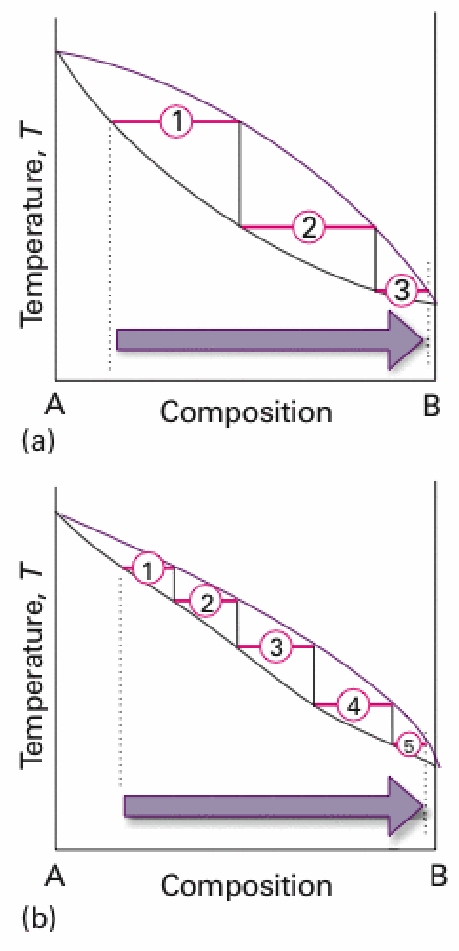
Consider what happens when a liquid of composition a_1 is heated. It boils when the temperature reaches T_2. Then the liquid has composition a_2 (the same as a_1) and the vapour (which is present only as a trace) has composition a_2'.



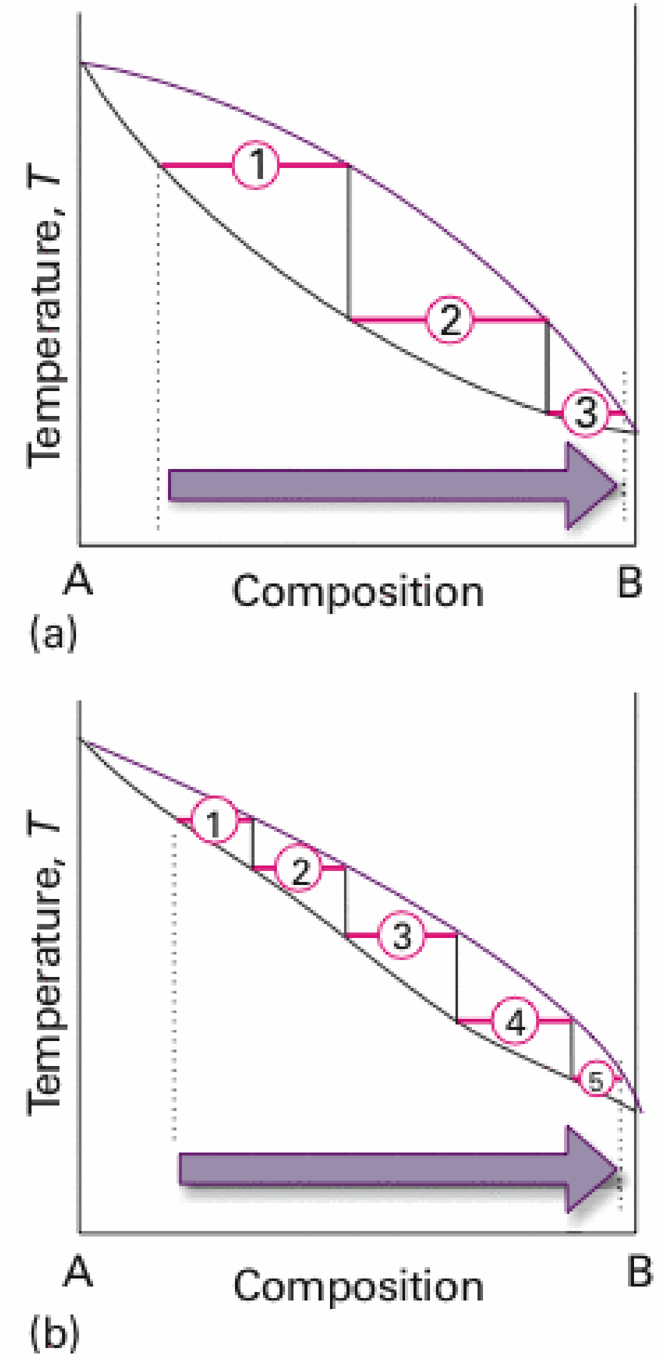
- The vapour is richer in the more volatile component A (the component with the ***lower*** boiling point). From the location of a_2,we can state the vapour's composition at the boiling point, and from the location of the tie line joining a_2 and a_2' we can read off the boiling temperature (T_2) of the original liquid mixture.

- In a **simple distillation**,the vapour is withdrawn and condensed. This technique is used to separate a volatile liquid from a non-volatile solute or solid. In **fractional distillation**, the boiling and condensation cycle is repeated successively. This technique is used to separate volatile liquids. We can follow the changes that occur by seeing what happens when the first condensate of composition a_3 is reheated. The phase diagram shows that this mixture boils at T_3 and yields a vapour of composition a_3',which is even richer in the more volatile component. That vapour is drawn off, and the first drop condenses to a liquid of composition a_4. The cycle can then be repeated until in due course almost pure A is obtained.

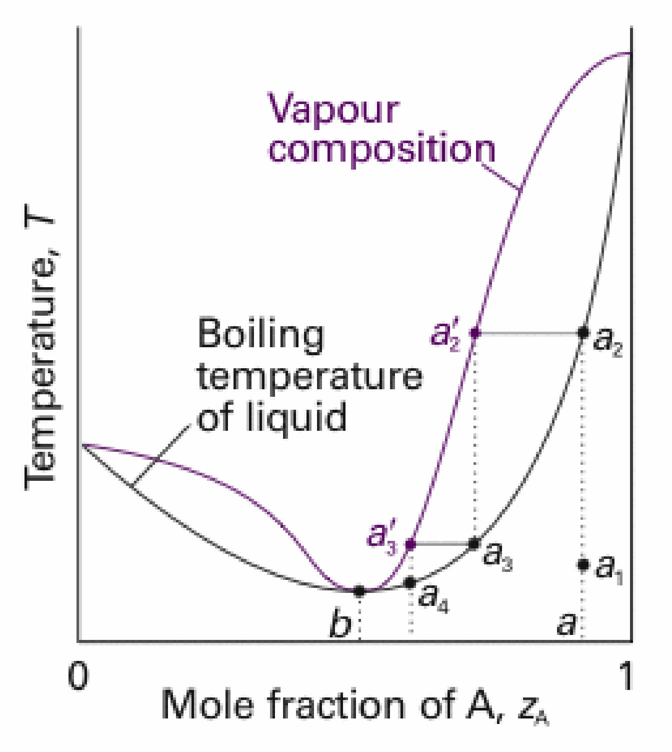
- The ***efficiency*** of a fractionating column is expressed in terms of the number of **theoretical plates**, the number of effective vaporization and condensation steps that are required to achieve a condensate of given composition from a given distillate. Thus, to achieve the degree of separation shown in the fractionating column must correspond to three theoretical plates. To achieve the same separation for the system shown in which the components have more similar partial pressures, the fractionating column must be designed to correspond to five theoretical plates.



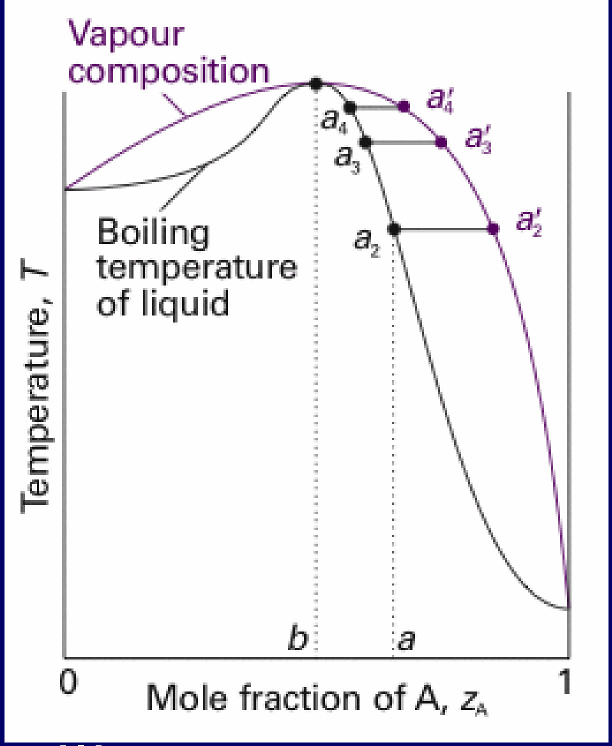
The number of theoretical plates is the number of steps needed to bring about a specified degree of separation of two components in a mixture. The two systems shown correspond to (a) 3, (b) 5 theoretical plates.



b) Azoetrope

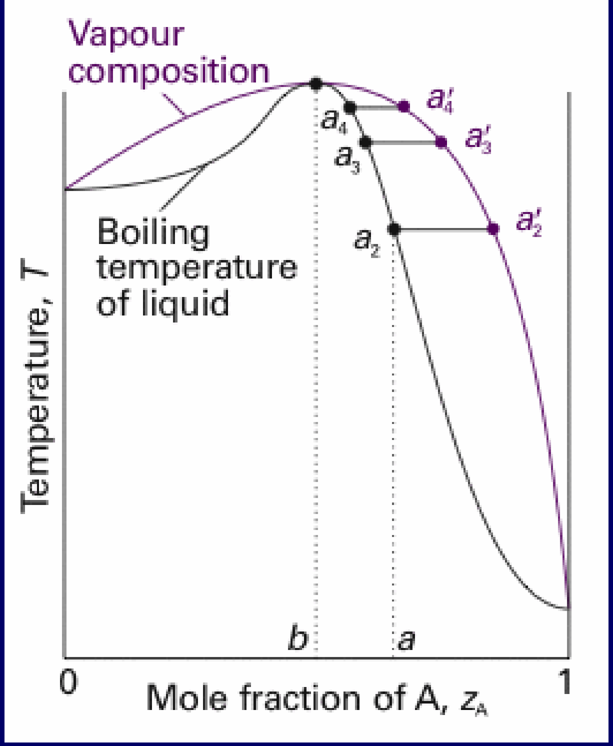


A low-boiling azeotrope. When the mixture at *a* is fractionally distilled, the *vapour* in equilibrium in the fractionating column moves towards *b* and then remains



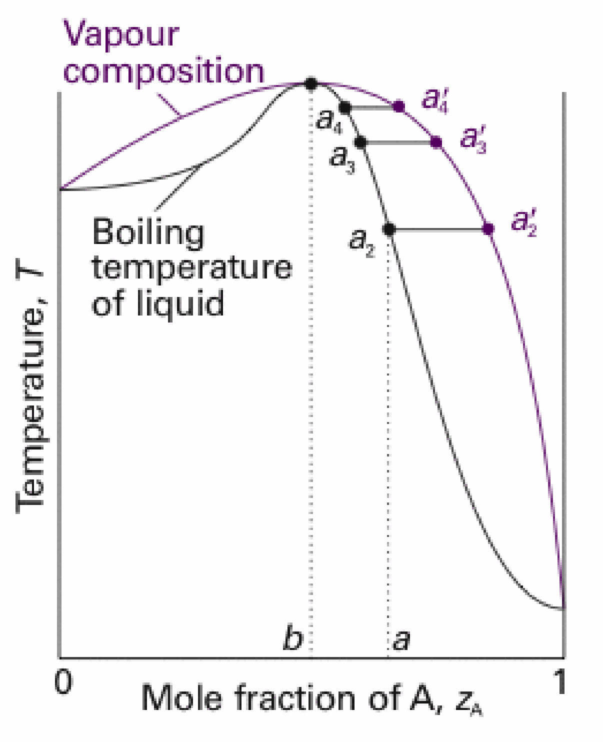
A high-boiling azeotrope. When the liquid of composition *a* is distilled, the composition of the *remaining* liquid changes towards *b* but no further.

The majority of (temperature – Composition) graphs resemble ideal types discussed so far. Some behave in different ways e.g. they show a maximum in the phase diagram . This occurs when interactions between A&B molecules reduce vapour pressure e.g. trichloromethane / propanone, nitric acid and water.

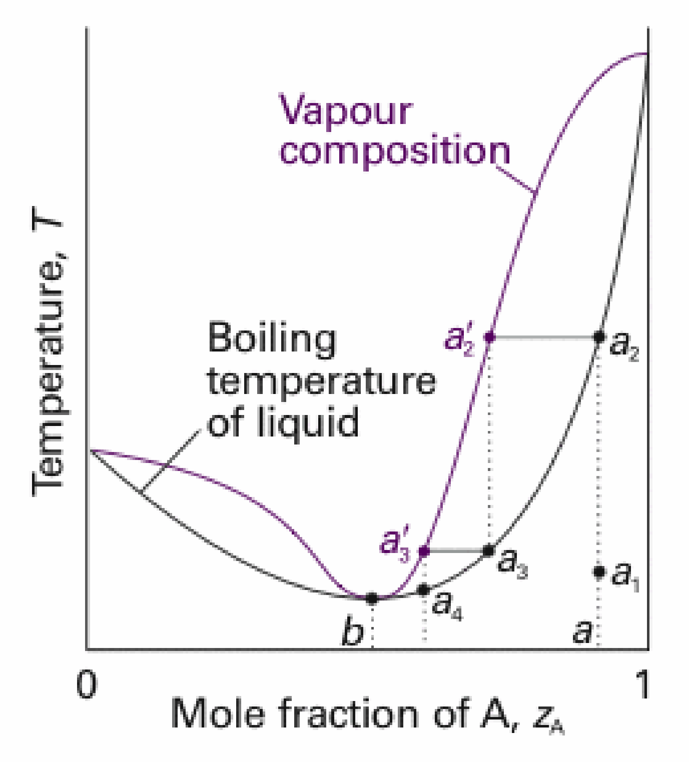


Consider a liquid of composition *a* on the ***right*** of the maximum . The vapour (at a_2') of the boiling mixture (at a_2) is ***richer*** in A. If that vapour is *removed (and condensed else where),*then the remaining liquid will move to a composition that is ***richer*** in B, such as that represented by a_3, and the vapour in equilibrium with this mixture will have composition a_3'. As that vapour is removed, the composition of the boiling liquid shifts to a point such as a_4, and the composition of the vapour shifts to a_4'. Hence, as evaporation proceeds, the composition of the remaining liquid shifts towards B as A is

The boiling point of the liquid rises, and the vapour becomes richer in B. When so much A has been evaporated that the liquid has reached the composition *b*, the vapour has the same composition as the liquid. Evaporation then occurs without change of composition. The mixture is said to form an **azeotrope**. When the azeotropic composition has been reached, distillation cannot separate the two liquids because the condensate has the same composition as the azeotropic liquid. One example of a zeotrope formation is hydrochloric acid/water, *which is azeotropic at 80 per cent by mass of water and boils unchanged at 108.6°C. IT is sold as such.*



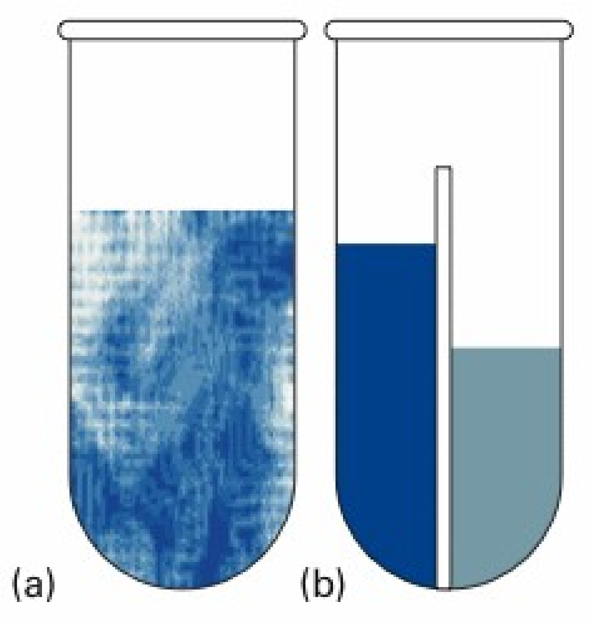
Phase diagrams showing a minimum indicate that the mixture is destabilized relative to the ideal solution, the A–B interactions then being unfavourable. Examples include dioxane/water and ethanol/water mixtures. The system shown in here is also azeotropic, but shows its azeotropy in a different way. Suppose we start with a mixture of composition a_1, and follow the changes in the composition of the vapour that rises through a fractionating column



.The mixture boils at a_2 to give a vapour of composition a_2'. This vapour condenses in the column to a liquid of the same composition (now marked a_3). That liquid reaches equilibrium with its vapour at a_3',which condenses higher up the tube to give a liquid of the same composition, which we now call a_4. The fractionation therefore shifts the vapour towards the azeotropic composition at b, but not beyond, and the azeotropic vapour emerges from the top of the column. An example is ethanol/water, which boils unchanged when the water content is 4 per cent by mass and the temperature is 78°C.

(c) Immiscible liquids

The distillation of **(a)** two immiscible liquids can be regarded as **(b)** the joint distillation of the separated components, and boiling occurs when the **sum** of the partial pressures equals the external pressure

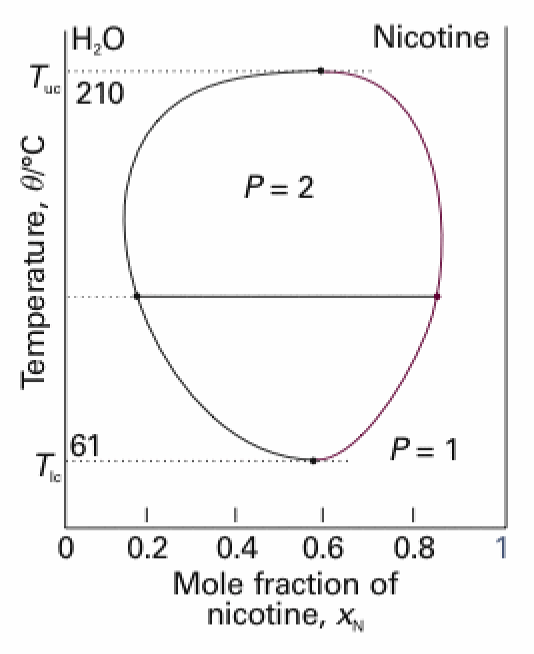


Distillation of two immiscible liquids, such as octane and water. At equilibrium, there is a tiny amount of A dissolved in B, and similarly a tiny amount of B dissolved in A: both liquids are saturated with the other component . As a result, the total vapour pressure of the mixture is close to $p = p_A^* + p_B^*$. If the temperature is raised to the value at which this total vapour pressure is equal to the atmospheric pressure, boiling commences and the dissolved substances are purged from their

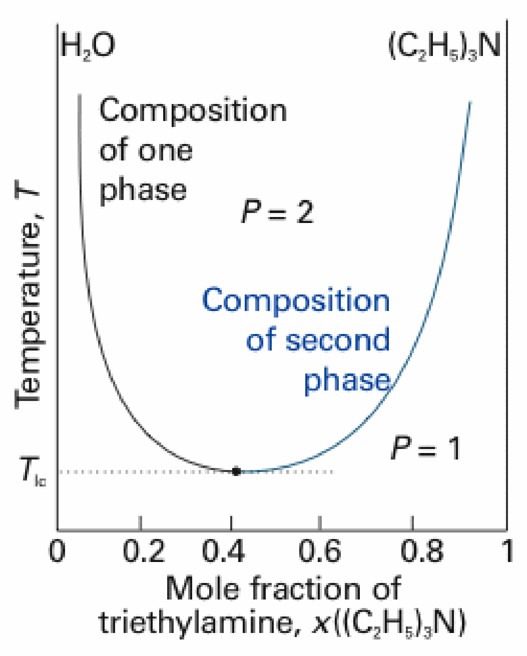
However, this boiling results in a vigorous agitation of the mixture, so each component is kept saturated in the other component, and the purging continues as the very dilute solutions are replenished. This intimate contact is essential: two immiscible liquids heated in a container would ***not*** boil at the same temperature. The presence of the saturated solutions means that the ‘mixture’ boils at a ***lower*** temperature than either component would alone because boiling begins when the total vapour pressure reaches 1 atm, not when either vapour pressure reaches 1 atm. This distinction is the basis of **steam distillation**, which enables some heat-sensitive, water-insoluble organic compounds to be distilled at a lower temperature than their normal boiling point.

Liquid–liquid phase diagrams

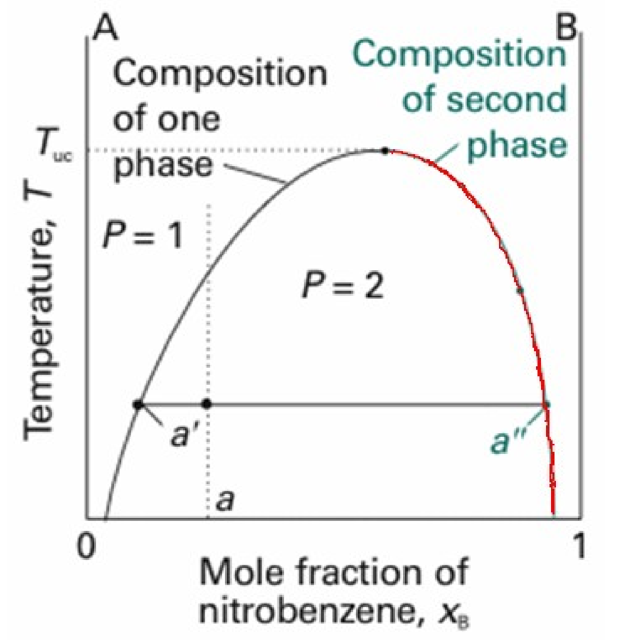
- Now we consider temperature–composition diagrams for systems that consist of pairs of **partially miscible** liquids, which are liquids that do not mix in all proportions at all temperatures. An example is hexane and nitrobenzene.
- The same principles of interpretation apply as to liquid–vapour diagrams. When $P = 2$, $F' = 1$ at const P, and the selection of a temperature implies that the compositions of the immiscible liquid phases are fixed. When $P = 1$ (corresponding to a system in which the two liquids are fully mixed), both the temperature and the composition may be adjusted.[see next slide for phase diagram]



Upper & lower solution T



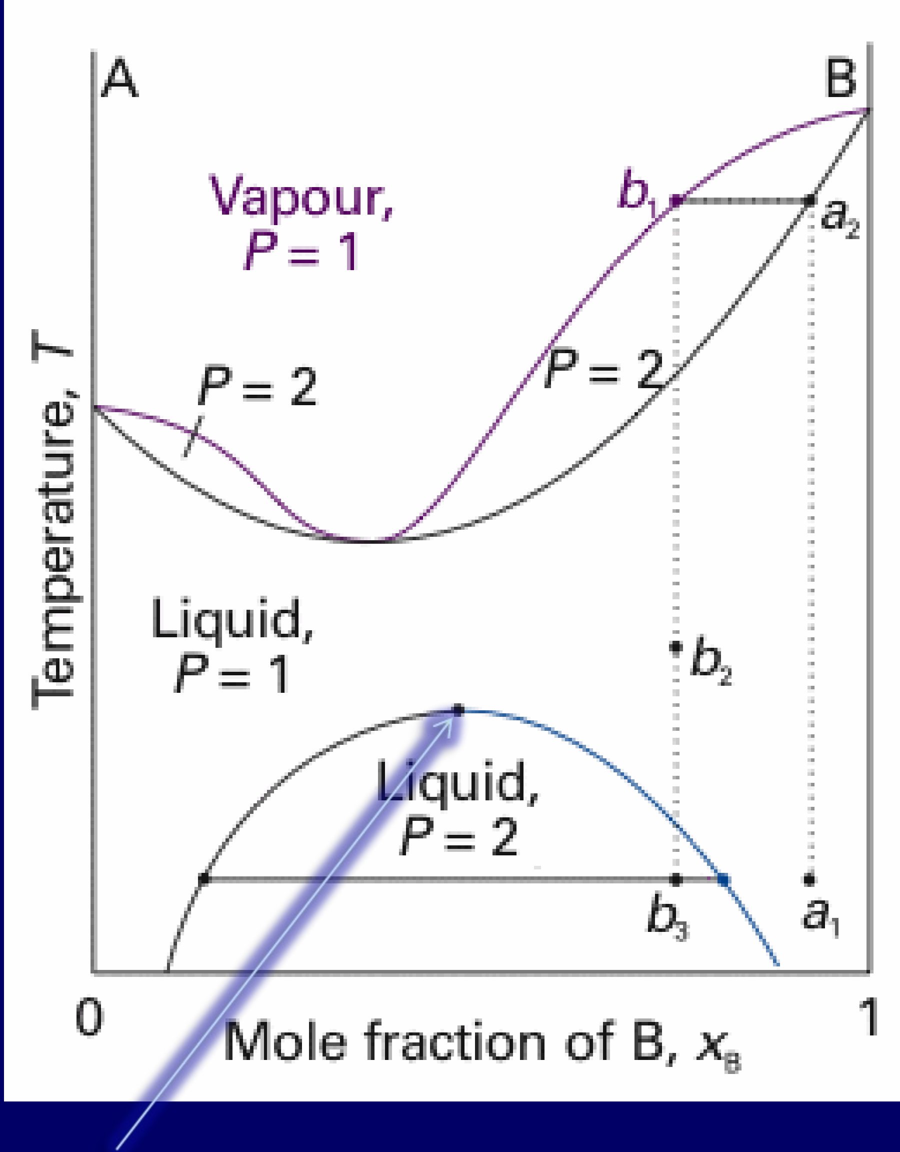
Lower critical solution T



Upper critical solution T

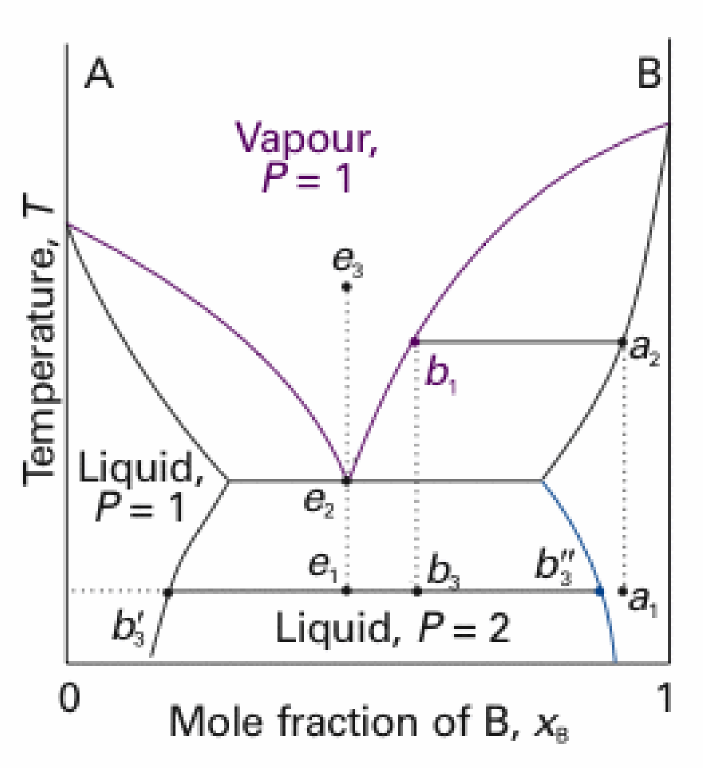
Distillation diagrams of such mixtures are rather complicated. But simple to follow .

Phase diagram for two components that become fully *miscible* before they boil. Distillation of a mixture of composition a_1 leads to a vapour of composition b_1,which condenses to the completely miscible single-phase solution at b_2. Phase separation occurs only when this distillate is cooled to a point in the two-phase liquid region, such as b_3. This description applies only to the first drop of distillate. If distillation continues, the composition of the remaining liquid changes. In the end, when the whole sample has evaporated and condensed, the composition is back to a_1.



Upper critical temperature

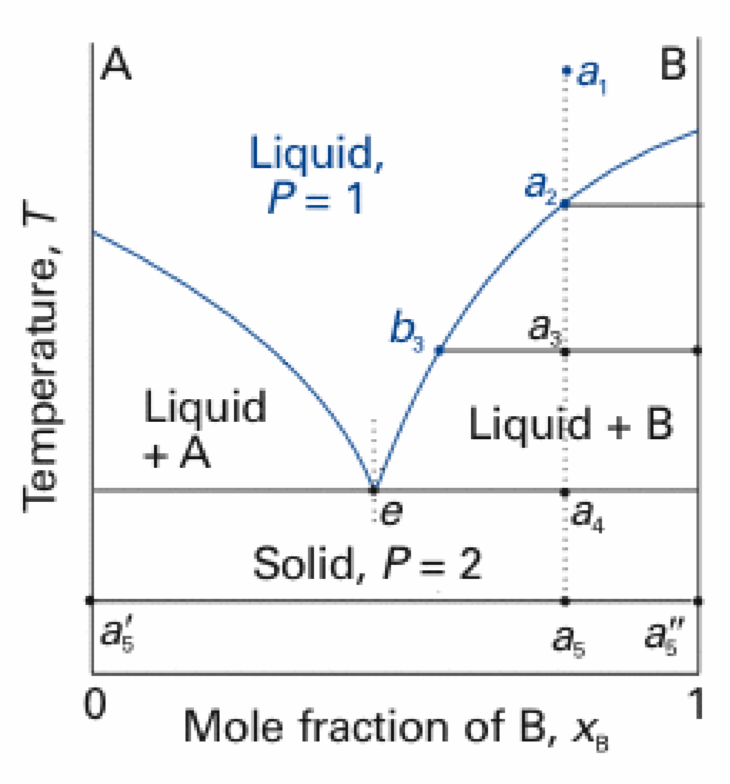
Next figure shows the second possibility, in which there is *no upper critical solution* temperature. The distillate obtained from a liquid initially of composition a_1 has composition b_3 and is a two-phase mixture. One phase has composition b_3' and the other has composition b_3''. The behaviour of a system of composition represented by the isopleth e is interesting. A system at e_1 forms two phases, which persist *(but with changing proportions*) up to the boiling point at e_2. The vapour of this mixture has the same composition as the liquid (the liquid is an azeotrope). Similarly, condensing a vapour of composition e_3 gives a two-phase liquid of the same overall composition. At a fixed temperature,



Liquid–solid phase diagrams

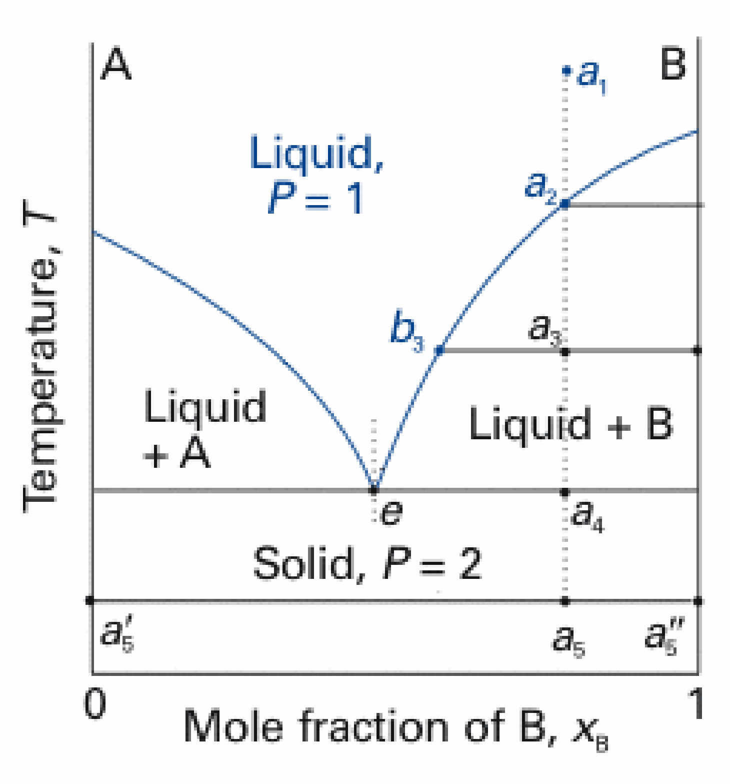
Knowledge of the temperature–composition diagrams for solid mixtures guides the design of important industrial processes, such as the manufacture of liquid crystal displays and semiconductors. we shall consider systems where solid and liquid phases may both be present at temperatures below the boiling point.

1. $a_1 \rightarrow a_2$. The system enters the two-phase region labelled ‘Liquid + B’. Pure solid B begins to come out of solution and the remaining liquid becomes richer in A



Continued

2. $a_2 \rightarrow a_3$. More of the solid forms, and the relative amounts of the solid and liquid (which are in equilibrium) are given by the lever rule. At this stage there are roughly equal amounts of each. The liquid phase is richer in A than before (its composition is given by b_3) because some B has been deposited.



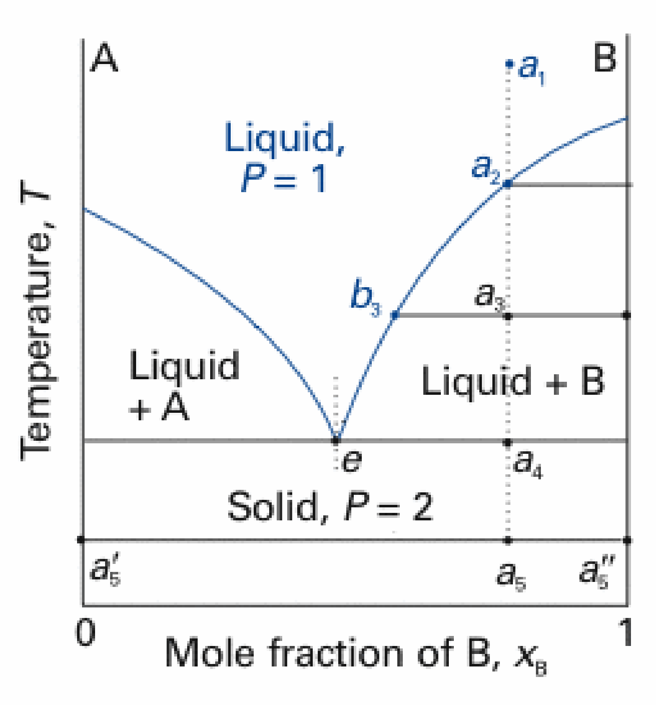
3. $a_3 \rightarrow a_4$. At the end of this step,there is less liquid than at a_3, and its composition is given by e. This liquid now freezes to give a two-phase system of pure B and pure A.

Eutectics

What is A eutectic? It is the mixture with the lowest melting point; a liquid with the eutectic composition freezes at a single temperature. A eutectic halt is a delay in cooling while the eutectic freezes. A solid with the eutectic composition melts, without change of composition, at the lowest temperature of any mixture.

e.g. The isopleth at *e* in the previous diagram

- Solutions of composition to the right of *e* deposit B as they cool, and solutions to the left deposit A: only the eutectic mixture (apart from pure A or pure B) solidifies at a single definite temperature ($F' = 0$ when $C = 2$ and $P = 3$) without gradually unloading one or other of the components from the liquid.



One technologically important eutectic is solder, which has mass composition of about 67 per cent tin and 33 per cent lead and melts at 183°C.

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